

CLAIMS

1. A method of producing a powder of barium titanate BaTiO_3 including solid solutions and doped compounds thereof, which powder is composed of non agglomerated ultrafine particles of tetragonal barium titanate of high density
5 corresponding to at least 90% of the intrinsic density of a large crystal of the corresponding compound, whose individual particles have an isotropic shape of given aspect ratio all particles being smaller than 1 micron and having a particle size distribution width measured by sedimentation* having a span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, where d_{v90} refers to a value such that 90% of the powder volume is made of smaller
10 sizes, d_{v10} refers to a value such that 10% of the powder volume is made of smaller sizes, and d_{v50} refers to the volume median diameter such that 50% of the powder volume is made of smaller sizes, and wherein the ratio of Ba:Ti including their substituents and dopants is very close to ideal stoichiometry, the method comprising:
- (a) carrying out a first stage reaction between reactants composed of compounds
15 of barium and titanium and optional selected substituents and dopants by preparing at room temperature a liquid-containing reaction mixture and subjecting the reaction mixture to reaction temperatures in the range 80°C , preferably 85°C , to boiling temperature, at a pressure of 1 bar, for a reaction period up to 20 minutes to produce a powder of barium titanate composed of
20 non-agglomerated ultrafine particles having a shape of said given aspect ratio and cubic structure, of low density corresponding at most to 90% of said intrinsic density, all particles being smaller than 1 micron and having a particle size distribution span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, and wherein the ratio of Ba:Ti including their substituents and dopants is very close to ideal
25 stoichiometry; and
- (b) subjecting the powder of cubic structure produced in step (a) to a second stage solvothermal post treatment at a temperature less than 400°C to convert the particles of low density to ultrafine particles of increased density corresponding to at least 90% of said intrinsic density, and converting the
30 isotropic, cubic-structure particles to tetragonal barium titanate particles while maintaining said given aspect ratio and maintaining the size of all particles below 1 micron, the particle size distribution span $(d_{v90}-d_{v10})/d_{v50}$ below 1, and the ratio of Ba:Ti including their substituents and dopants very close to ideal stoichiometry.
- 35 2. The method of claim 1, wherein the produced mixed oxide is a solid solution of composition $\text{Ba}_{(1-x)}\text{A}_x\text{Ti}_{(1-y)}\text{B}_y\text{O}_3$, where the mole fractions x and y are each

* All measurements of particle size distributions by sedimentation in the description and claims are made using a BI-XDCP Particle Sizer instrument.

- in the range between 0 and 1, preferably larger than 0.03, A is at least one divalent metal selected from calcium, cadmium, europium, magnesium, lead, radium, strontium and zinc and B is least one tetravalent metal selected from cerium, cobalt, iron, hafnium, molybdenum, lead, praseodymium, plutonium, ruthenium, tin, thorium, uranium, vanadium and zirconium.
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3. The method of claim 2, wherein the produced powder is a doped solid solution of composition $Ba_{(1-x-a)}A_xX_aTi_{(1-y-b)}B_yY_bO_3$, where the mole fractions x and y are in the range of 0 to 1, preferably larger than 0.03, the mole fractions a and b are in the range 0 to 0.2, preferably below 0.05, A represents one or more of said divalent metals, B represents one or more of said tetravalent metals, and X and Y each represent one or more other metals selected from the group consisting of calcium, lanthanum, rare earth elements, lithium, magnesium, yttrium, niobium, tantalum, gallium, molybdenum, tungsten, manganese, copper, iron, cobalt, nickel, chromium, zinc, aluminium, silicon, antimony, lead, bismuth, boron and mixtures thereof.
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4. The method of claim 2, wherein the produced powder is a doped barium titanate $Ba_{(1-a)}X_aTi_{(1-b)}Y_bO_3$, where the mole fractions a and b are in the range between 0 to 0.2, preferably below 0.05, and X and Y each represent one or more metals selected from the group consisting of calcium, lanthanum, rare earth elements, lithium, magnesium, yttrium, niobium, tantalum, gallium, molybdenum, tungsten, manganese, copper, iron, cobalt, nickel, chromium, zinc, aluminium, silicon, antimony, lead, bismuth, boron and mixtures thereof.
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5. The method of claim 3 or 4, wherein the dopant elements X and/or Y are introduced as reagents in step (a) to ensure homogeneous dopant distribution within the structure, and/or as reagents in step (b) to ensure a gradient of dopant concentration from the particle surface to the particle core.
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6. The method of claim 1, wherein the produced powder is undoped and non-substituted barium titanate $BaTiO_3$.
7. The method of any preceding claim, wherein the tetragonal particles produced in step (b) have an isotropic and faceted individual particle shape, in particular a cube-like shape.
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8. The method of claim 7, wherein the powder produced in step (b) has more than 50% and preferably more than 80 or 90% of cube-like shape tetragonal particles.
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9. The method of claim 7 or 8, wherein the powder produced in step (b), or after a subsequent heat treatment, has 5-95% of individual particles with an isotropic and faceted individual particle shape, in particular a cube-like shape.

10. The method of claim 7, 8 or 9, wherein the cubic-structure particles produced in step (a) have a generally spherical shape.
11. The method of any preceding claim, wherein step (b) is followed by a heat treatment during which part or all of the particles change shape.
- 5 12. The method of claim 11, wherein after the heat treatment 5-80%, 5-50% or 5-20% of the individual particles retain an isotropic faceted shape in particular a cube-like shape.
- 10 13. The method of any one of claims 1 to 12, wherein step (a) is performed by preparing a dispersion, emulsion, suspension or gel of the reaction mixture at room temperature in particular by mixing a mixture of salts, alkoxides or hydroxides of barium and titanium optionally with NaOH, KOH, TMAH or ammonia.
- 15 14. The method of claim 13 when depending on claim 5, wherein dopant reagent(s) is/are introduced to the dispersion, emulsion, suspension or gel in the form of salts, alkoxides, organic compounds or hydroxides of the dopant elements to produce the doped solid solution.
- 20 15. The method of any preceding claim, wherein step (a) is performed using a continuous reactor or a reactor that discontinuously processes reaction volumes up to 1 litre.
- 25 16. The method of claim 15, wherein step (a) is performed using a discontinuous fed-batch reactor of up to 1 litre reaction volume, or using a continuous mixed suspension-mixed product removal (MSMPR) reactor of up to 1 litre residence volume.
- 30 17. The method of claim 15, wherein step (a) is performed using a tubular reactor.
- 35 18. The method of claim 17, wherein step (a) is performed using a Segmented Flow Tubular Reactor wherein reaction volumes are separated by a segmenting fluid that is not miscible with the reaction mixture.
19. The method of any preceding claim, wherein step (b) is performed by adding the barium titanate powder produced in step (a) to an aqueous solution at pH above 9 or to a non-aqueous solution of at least one metal compound to produce a suspension, and subjecting the suspension to a solvothermal post treatment at a pressure above 1 bar and a temperature between 100°C and 400°C, preferably in the range 200-350°C, for a residence period of 2 to 20 hours.
20. The method of any preceding claim, wherein a large quantity of low density barium titanate is produced by repeating step (a) with small volumes of the reaction mixture that each yield small quantities of the low density barium

titanate that are collected to form said large quantity, and subjecting said large quantity of low density barium titanate to the second stage solvothermal post treatment.

21. The method of any preceding claim, wherein the span of particle size distribution is maintained or decreased from step (a) to step (b), with a shift of the particle size distribution (d_{v10} , d_{v50} , d_{v90}) towards higher sizes after the solvothermal post-treatment of step (b).
22. The method of any preceding claim wherein in step (a) the reaction mixture is heated from room temperature to the reaction temperature in less than 3 minutes, optionally with stirring.
23. The method of any preceding claim, wherein step (b) is performed using a hydrothermal apparatus.
24. A powder of barium titanate $BaTiO_3$ including solid solutions and doped compounds thereof, that is obtainable by the method of any preceding claim, which powder is composed of non agglomerated ultrafine particles of tetragonal barium titanate of high density corresponding to at least 90% of the intrinsic density of a large crystal of the corresponding compound, of which at least 50%, preferably at least 80 or 90% of the individual particles have an isotropic faceted shape, in particular a cube-like shape, all particles being smaller than $1\ \mu m$ and having a particle size distribution measured by sedimentation having a span $(d_{v90}-d_{v10})/d_{v50}$ less than 1, where d_{v90} refers to a value such that 90% of the powder volume is made of smaller sizes, d_{v10} refers to a value such that 10% of the powder volume is made of smaller sizes, and d_{v50} refers to the volume median diameter such that 50% of the powder volume is made of smaller sizes, and wherein the ratio of Ba:Ti including their substituents and dopants is very close to ideal stoichiometry.
25. A powder of barium titanate $BaTiO_3$ including solid solutions and doped compounds thereof, that is obtainable by the method of any of claims 1 to 24, which powder is composed of ultrafine particles, wherein no agglomerates are bigger than $1\ \mu m$, preferably no bigger than $0.8\ \mu m$, having:
 - (a) a primary particle size distribution determined from image analysis with a median number diameter d_{n50} comprised in the range 0.005 to $0.250\ \mu m$, a maximum primary particle size of $0.5\ \mu m$, a number size distribution span $(d_{n90}-d_{n10})/d_{n50}$ of 0.8 and below, and a geometric standard deviation σ_g ($=d_{n50}/d_{n84}$) from 0.75 to <1 ,
 - (b) a particle size distribution measured by sedimentation with a median volume diameter d_{v50} comprised in the range 0.01 to $0.5\ \mu m$, without any hard agglomerate bigger than $0.8\ \mu m$, a volume size distribution span $(d_{v90}-$

- d_{v10}/d_{v50} less than 0.95 and a geometric standard deviation $\sigma_g (=d_{v50}/d_{v84})$ from 0.70 to <1 ,
- (c) a factor of agglomeration ($F_{AG} = d_{v50}/d_{BET}$) smaller than 2.1, preferably smaller than 1.6,
- 5 (d) a ratio between the sedimentation d_{v50} and the image analysis d_{v50} in the range 1.0 to 1.5,
- (e) a tetragonal structure,
- (f) a density of at least 90% of the intrinsic density of a large crystal of the corresponding compound,
- 10 (g) a hydroxyl content less than 1 wt%, and
- (h) a ratio of Ba:Ti including their substituents and dopants equal to 1.00 plus or minus 1 atomic percent.
26. The powder of claim 25 wherein at least 50 %, preferably 80%, more preferably 90% of individual particles have an isotropic and faceted individual particle shape, in particular a cube-like shape.
- 15 27. The powder of claim 25 or 26 which is undoped and non-substituted tetragonal barium titanate $BaTiO_3$ of which at least 80%, preferably at least 90%, of the individual particles have a cube-like shape.
28. A method of producing a body, in particular a ceramic body, comprising producing barium titanate powder by the method of any one of claims 1 to 23, and forming the powder into a body with or without binding agents, in particular by the application of pressure and heat separately or together.
- 20 29. The method of claim 24 wherein the body is a capacitor.
30. A method of producing a film, coating or layer of barium titanate, comprising producing barium titanate powder by the method of any one of claims 1 to 28, and forming the powder into a film, coating or layer by tape casting, doctor blading, screen-printing, electrodeposition, dip coating, spin coating or thermal spraying and optionally applying heat to the as-produced film, coating or layer.
- 25 31. The method of claim 30 wherein the powder is formed as a coating on a substrate or a layer in a multilayer structure.
- 30 32. The method of claim 34 wherein the barium titanate powder is formed as a non-supported film.
33. A method of producing a dispersion, suspension, emulsion or gel of a barium titanate powder in a fluid medium, comprising producing barium titanate powder by the method of any one of claims 1 to 28, and maintaining the
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particles in suspension at the end of step (b) and/or mixing the produced powder with the fluid medium to produce the dispersion, suspension, emulsion or gel.